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Electrodeposition of Ni Catalyst on Tungsten Substrates and Its Effect on the Formation of Carbon Nano- and Micro-coils

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ABSTRACT

Carbon micro-coils and nano-coils were produced in high yield from nickel catalyst particles electrochemically deposited onto tungsten substrates. Various electrochemical deposition techniques were used to produce the nickel catalyst particles. These particles catalyzed the chemical vapor deposition (CVD) of acetylene at 800°C, resulting in growth of carbon micro- and nano-coils. Linear-sweep (cyclic) voltammetry produced catalyst particles which resulted in single-filament coils intermixed with thin nanotubes over most of the substrate surface. Passing the same amount of charge by constant current electrolysis produced nickel particles that decomposed carbon but did not grow coils. Catalyst particles deposited by constant current electrolysis grew nanocoils similar to linear-sweep voltammetry but in small, localized, high-yield patches. The coils produced were either spring-like micro-coils of low pitch and large diameter or rope-like nano-coils of higher pitch and smaller diameter. High-resolution transmission electron microscopy (HRTEM) showed typical graphite fringes in the filaments, but did not reveal an internal tubular structure. Catalyst particles were often detected at the ends of the coils.

INTRODUCTION

Their uniqueness and interesting properties have prompted many researchers to investigate carbon coils [1-4]. Not unlike other carbon micro- and nano-structures, carbon coils have many potential applications such as micro-springs, micro-sensors, magnetic beam generators, and electromagnetic shielding materials [5]. For some applications the substrate on which these coils are grown would play an important role. Tungsten is a very practical substrate because of its strength, high melting point, and use as a high-performance material. Various catalyst-substrate combinations have been used to grow carbon micro- and nano-coils, but we are the first to produce carbon coils from nickel catalyst electrochemically deposited onto tungsten. In this research, the effects of various electrochemical techniques used to deposit nickel onto tungsten substrates were investigated.

EXPERIMENT

Nickel (Ni) catalyst particles were electrochemically deposited onto tungsten (W) by three different electrochemical deposition techniques: linear-sweep voltammetry, constant current

electrolysis, and constant potential electrolysis. The electrolyte solution was 1.0 M in NaCl, 1.0 M in NH_4Cl, and 10 mM in $Ni(NO_3)_2 \cdot 6H_2O$, and was basified to pH 8.3 by addition of concentrated NH_4OH [6]. A three-compartment glass electrochemical cell was used, and the electrolyte was deoxygenated by sparging with N_2 before Ni deposition. The working electrode was a polished W rod of 4 mm in diameter, cleaned in an ultrasonic bath prior to deposition. The reference electrode was a Ag wire immersed in saturated aqueous KCl solution and isolated by a porous vycor plug, and is referred to here as the Ag/AgCl reference. The auxiliary electrode was a coiled Pt wire.

Using the linear-sweep voltammetry technique, Ni was deposited by sweeping the potential of the working electrode linearly from -0.25 V to -1.2 V vs. Ag/AgCl at a scan rate of 30 mV/s. The presence of Ni was verified by reversing the scan from -1.2 V back to -0.25 V and observing a stripping peak at -0.38 V. The presence of this stripping peak indicates the removal of Ni from the electrode. The potential of the W electrode was scanned once again from -0.25 V to -1.2 V vs. Ag/AgCl, then reversed, stopping at a potential of -0.75 V to complete deposition without removing any Ni. Using the constant current electrolysis technique, Ni was deposited by applying a constant current for a designated time interval. Using constant potential electrolysis, a potential of –1.5 V was applied to the working electrode for different time intervals. All deposition processes were controlled by a computer-interfaced potentiostat/galvanostat designed in-house.

To grow carbon nano-coils the W substrates were placed in a ceramic boat, which was inserted into a CVD chamber. The chamber was heated to 700 °C where 385 sccm (standard cubic centimeters per minute) H_2 was introduced for 15 minutes to activate the Ni catalyst. The samples were then heated to 800 °C at which both 385 sccm H_2 and 25 sccm C_2H_2 were introduced for 10, 15, or 20 minutes. The pressure was maintained at 100 mbar throughout the growth process. After cooling to room temperature, the samples were removed from the reaction chamber. Black soot visible on the W surface indicated deposition of carbon on the substrate.

An FEI 611 focused ion beam (FIB) microscope and an ISI-SS40 scanning electron microscope (SEM) were used to characterize the morphologies of the samples. An FEI Tecnai F-20 field emission high-resolution transmission (and scanning transmission) electron microscope (HRTEM/STM) equipped with a high angle annular dark field detector (HAADFD) and an energy dispersive x-ray (EDX) spectrometer was used to examine the internal structures and the chemical compositions of the coils. TEM samples were prepared by carefully scratching some soot from the W substrates and dispersing it in a small amount of acetone, several drops of which were then applied to a lacy-carbon coated copper TEM grid.

RESULTS AND DISCUSSION

When the above experiment was run using a clean W substrate with no deposited Ni, no growth of any carbon structures occurred. This indicates pure W does not catalyze carbon coil or nanotube growth. Both nanotubes and carbon coils, however, were synthesized via chemical vapor deposition of acetylene at 800 °C when Ni was electrochemically deposited onto the W substrates, identifying the deposited Ni particles as the growth catalyst. Figure 1 below shows coils produced from catalyst deposited by the linear-sweep voltammetry technique. Thin carbon nanotubes, having diameters between 10 and 50 nm, are visible. These were often co-synthesized with the carbon coils, growing in among them. This technique deposited Ni catalyst particles in a fairly uniformly distributed fashion on the W surface.

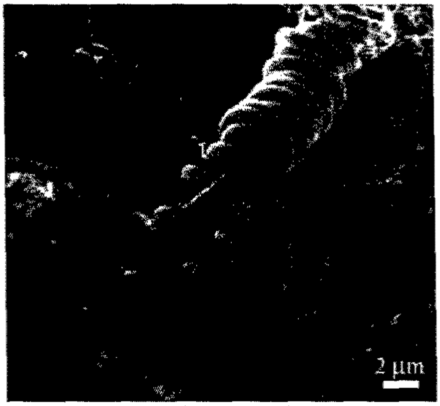

Figure 1. Co-production of carbon coils and carbon nanotubes

This growth was fairly uniform over the substrate surface. Under the same growth conditions we also observed the production of carbon coils from pure Ni, indicating the Ni itself is important in coil growth. The presence of Ni catalyst particles is necessary for growth, but the particle's size and shape seem to determine the actual growth structure.

Figure 2(a) shows a micro-coil grown from Ni nanoparticles deposited via linear-sweep voltammetry. These micro-coils had diameters between 1 µm and 5 µm, while the filament thicknesses were between 250 and 700 nm. Rope-like nano-coils were also produced by this deposition method, as seen in Figure 2(b). The diameters of these coils were between 50 and 250 nm and the average thickness of their filaments was less than 100 nm. Comparing Figures 2(a) and 2(b) one easily sees the pitch of the micro-coils tends to be much larger and much more irregular than that of the nano-coils. The presence of Ni, which was often found at the tip of the coils, was confirmed by energy dispersive x-ray analysis (EDX).

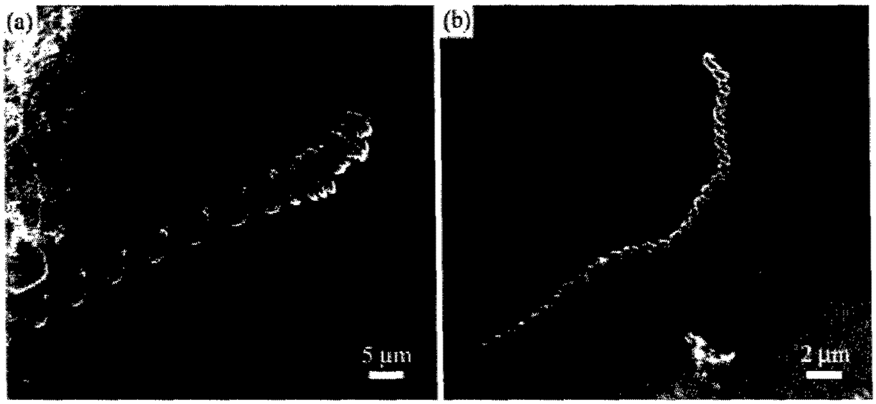

Figure 2. FIB images of a micro-coil (a) and a nano-coil (b).

The production and yield of carbon coils, however, was not always the same. Changing the electrodeposition technique used to deposit Ni had a noticeable effect on coil production. In this study we have shown that different techniques of electrochemical Ni catalyst deposition influence the production of carbon coils. When constant potential electrolysis was used to deposit the catalyst particles, growth of carbon coils was dependent upon deposition time. Our research indicates carbon coils are grown from large catalyst clusters [6], thus a longer deposition time would be needed for the Ni particles to grow large enough to be able to produce nano- and micro-coils. Other studies have shown that the size of electrochemically deposited Ni catalyst particles is controllable by adjusting various deposition parameters such as current, potential, and deposition time [7-8], specifically a constant potential applied for a longer time interval yields larger Ni clusters [7]. This is in agreement with our coil growth hypothesis. The constant potential technique worked only when done over a long enough time to grow large clusters. Figure 3(a) below shows coil production resulting from Ni deposition by constant potential electrolysis.

The linear-sweep voltammetry technique applies a linearly-varying potential to the working electrode for a relatively long time interval (~1 minute). As a result, deposited Ni particles have plenty of time to nucleate into large clusters. This explains why this deposition method was always effective in growing carbon coils. The constant current electrolysis technique, on the other hand, applied a current to the working electrode for a much shorter time, 2 seconds or less, in order to pass the same amount of charge as was passed in the linear-sweep voltammetry technique. This allowed much less time for Ni particles to cluster. Consequently this deposition technique produced few, dispersed carbon nanotubes from small Ni clusters, but no carbon coils. When using the constant potential electrolysis technique, whether or not the deposited Ni particles produced carbon coils depended on deposition time. Deposition over a short time interval resulted in no coil growth, while a longer deposition time produced carbon coils. Results similar to those from the linear-sweep voltammetry technique were observed by applying a potential of -1.2 V for 20 s. The main difference was that the Ni particles were not deposited evenly over the substrate surface, but instead in small bunches.

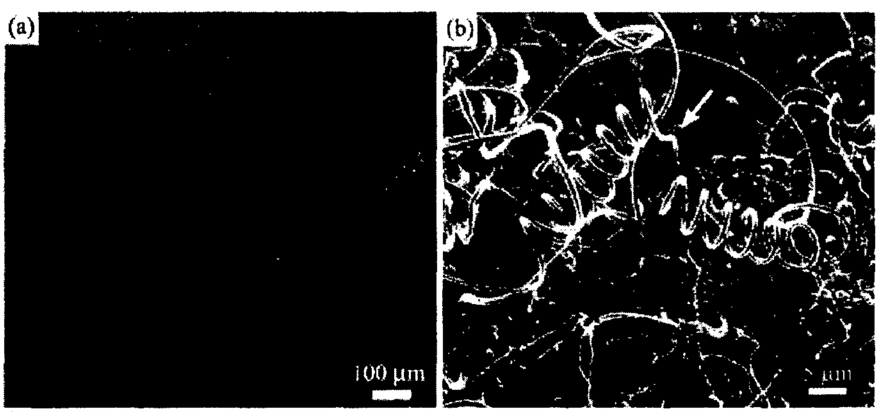

Figure 3. (a) Localized, high-yield coil growth resulting from constant potential electrolysis catalyst deposition. (b) A close-up view of Figure 3(a), showing a high-yield of coils.

This non-uniform distribution of catalyst grew patches of coils and carbon nanotubes. The coil yield in these patches was slightly higher than from linear-sweep voltammetry (Figure 3 above). When the deposition time was reduced to 4 seconds, smaller Ni catalyst particles were deposited, growing thin carbon nanotubes but no coils.

Generally, carbon coils exhibited exclusively right- or left-handed helicity, but some coils actually changed helicity during growth. An occurrence of this in a micro-coil is indicated by the arrow in Figure 3(b). An example of a nano-coil changing helicity is shown by the arrow in Figure 4.

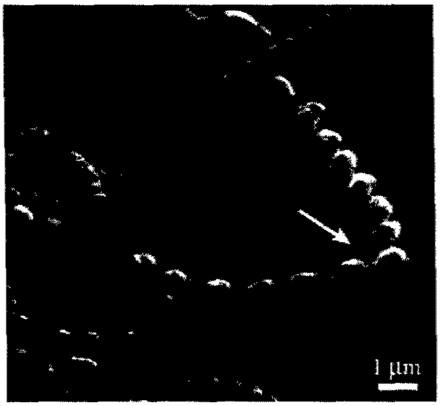

Figure 4. Changing helicity in a carbon nano-coil.

HRTEM images showed the internal structure of a carbon micro-coil to be typical graphite fringes, but revealed no internal tubular structure. Graphite fringes in a micro-coil are shown below in Figure 5.

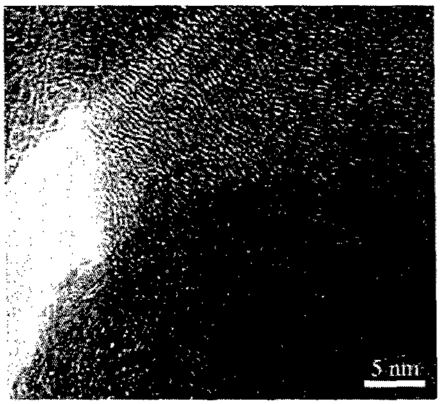

Figure 5. HRTEM image revealing the internal structure of a carbon coil

CONCLUSIONS

Carbon micro- and nano-coils were grown from Ni catalyst particles via the chemical vapor deposition of acetylene at 800 ºC. Different Ni deposition techniques and their effects on the production of carbon coils were investigated. It was found that both linear-sweep voltammetry and constant potential electrolysis were effective in producing carbon coils, whereas constant current electrolysis yielded only thin carbon nanotubes. These results, however, do not imply the constant current technique cannot deposit coil-producing catalyst particles. Our results show electrochemical deposition techniques that deposit sufficiently large catalyst particles produce carbon micro- and nano-coils. A constant potential was applied for both 4 and 20 s in the constant potential technique, while the linear-sweep technique took more than one minute to deposit Ni. The constant current technique, on the other hand, in order to pass the same amount of charge as was passed in the linear-sweep voltammetry technique, applied a constant current for only a very short time period (less than two seconds). This resulted in very little time for Ni catalyst particles to nucleate. If this technique were used to apply the same current for a longer time, Ni particles large enough to produce carbon coils should be produced. Based on these results, this study suggests that adjusting the catalyst deposition parameters can influence the production of coils on W substrates. Additional research needs to be done to determine the role of the substrate on the production of carbon coils.

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